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Diffuse Neutron Scattering Signatures of Rough Films

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ABSTRACT

Patterns of diffuse neutron scattering from thin films are calculated from a perturbation expansion based on the distorted-wave Born approximation. Diffuse fringes can be categorised into three types: those that occur at constant values of the incident or scattered neutron wavevectors, and those for which the neutron wavevector transfer perpendicular to the film is constant. The variation of intensity along these fringes can be used to deduce the spectrum of surface roughness for the film and the degree of correlation between the film's rough surfaces.

1. INTRODUCTION

In a recent paper [1], I derived a series of expressions that describe the way in which neutrons, incident at grazing angles on the upper surface of a planar thin film, are diffusely scattered by roughness of the film's surfaces. Unfortunately, these expressions involve the sum of many terms and do not lend themselves readily to an intuitive understanding of the patterns of diffuse scattering that may be obtained with a rough film. The purpose of this paper is to present examples of the signatures of different aspects of surface roughness, as recorded by neutron (or x-ray) scattering.

Elements in a pattern of diffuse neutron scattering obtained with a rough thin film may have three possible physical origins. The simplest I shall call the Newton effect because it is the analogue of a phenomenon first reported by Sir Isaac Newton [2] for light. When a film is illuminated, irregularities of the upper (illuminated) surface scatter part of the incident radiation which is then reflected by the film/substrate interface. The same irregularities also scatter radiation that traverses the upper surface on its way out of the film, having been reflected from the film/substrate interface. Radiation that has followed these two paths produces an interference pattern of fringes whose spacing is determined by the film thickness. It is as if there were two radiating sources that interfered—the rough surface and its image in the film/substrate interface. The observed fringes are a result of the fact that the wave field at the rough film surface is the sum of incident and reflected waves, whose phases are related by the film thickness. The loci of the interference fringes are determined by the perpendicular components of the wavevectors of the incident (k_{1z}) and scattered (k_{2z}) neutrons, not by a combination of these wavevectors.

The second source of diffuse scattering arises from radiation that penetrates the film and is scattered by its rough lower surface. This source of scattering gives rise to one or two fringes whose loci are also determined by k_{1z} and k_{2z} separately. The fringes arise because of structure in the film transmittance around the wavevector for critical reflection.

The third source of diffuse scattering arises when there is some degree of correlation between the two rough surfaces of the film. In this case, each fringe of diffuse scattering occurs at a constant value of the wavevector transfer, q_z ($= k_{1z} + k_{2z}$), perpendicular to the film's surfaces. The fringes arise because of the phase difference between waves scattered by the two rough surfaces; the distortion of the incident waves from their original plane-wave form by the film is a secondary effect in this case.

2. EXPRESSION FOR THE DIFFUSE SCATTERING

The expressions derived in [1] for the various contributions to the diffuse scattering cross section, ($d\sigma/d\Omega$), per unit area of a thin, rough film are reproduced below to facilitate the discussion of this paper. Eqn (1) is the Newton term, eqn (2) describes scattering from the lower film surface, and eqn (3) arises from correlations between roughness of the two surfaces of the film.

$$\left.\frac{d\sigma}{d\Omega}\right)_{upper} = (\beta_F)^2 \sum_{n=1}^{n=6} \frac{(-1)^{n+1}}{f_n g_n} F_n e^{-(f_n^2 + g_n^2)\sigma^2/2} \times \int dx \int dy\, e^{-i\vec{\kappa}\cdot\vec{\rho}} \left\{\exp\left[(-1)^{n+1} f_n g_n \langle\xi(\rho)\xi(0)\rangle\right] - 1\right\} \tag{1}$$

$$\left.\frac{d\sigma}{d\Omega}\right)_{lower} = (\beta_S - \beta_F)^2 |T_F(k_{1z})|^2 |T_F(k_{2z})|^2 e^{-(\gamma^2 + \gamma^{*2})\sigma_2^2/2} \times \int dx \int dy\, e^{-i\vec{\kappa}\cdot\vec{\rho}} \left\{\exp\left[|\gamma|^2 \langle\eta(\rho)\eta(0)\rangle\right] - 1\right\} \tag{2}$$

$$\left.\frac{d\sigma}{d\Omega}\right)_{corr} = 2(\beta_S - \beta_F)(\beta_F) \sum_{n=1}^{n=4} \frac{(-1)^{n+1}}{f_n \gamma} G_n e^{-(f_n^2\sigma_1^2 + \gamma\sigma_2^2)\sigma^2/2} \times \mathrm{Re}\left[\int dx \int dy\, e^{-i\vec{\kappa}\cdot\vec{\rho}} \left\{\exp\left[(-1)^{n+1} f_n \gamma \langle\eta(\rho)\xi(0)\rangle\right] - 1\right\}\right] \tag{3}$$

where

$$f_1 = f_2 = f_5 = f_6 = g_1 = g_2 = k_{1z} + k_{2z} \tag{4a}$$

$$f_3 = f_{42} = g_3 = g_4 = g_5 = g_6 = k_{1z} - k_{2z} \tag{4b}$$

$$F_1 = 1 + |R_F(k_{1z})|^2 \, |R_F(k_{2z})|^2 \tag{5a}$$

$$F_2 = 2 \text{ Re } \{R_F(k_{1z}) \, R_F(k_{2z})\} \tag{5b}$$

$$F_3 = |R_F(k_{1z})|^2 + |R_F(k_{2z})|^2 \tag{5c}$$

$$F_4 = 2 \text{ Re } \{R_F^*(k_{1z}) \, R_F(k_{2z})\} \tag{5d}$$

$$F_5 = 2 \text{ Re } \left\{ R_F^*(k_{2z}) + R_F(k_{2z}) |R_F(k_{1z})|^2 \right\} \tag{5e}$$

$$F_6 = 2 \text{ Re } \left\{ R_F^*(k_{1z}) + R_F(k_{1z}) |R_F(k_{2z})|^2 \right\} \tag{5f}$$

$$G_1 = T_F(k_{1z}) \, T_F(k_{2z}) \tag{6a}$$

$$G_2 = T_F(k_{1z}) \, T_F(k_{2z}) \, R_F^*(k_{1z}) \, R_F^*(k_{2z}) \tag{6b}$$

$$G_3 = T_F(k_{1z}) \, T_F(k_{2z}) \, R_F^*(k_{2z}) \tag{6c}$$

$$G_4 = T_F(k_{1z}) \, T_F(k_{2z}) \, R_F^*(k_{1z}) \tag{6d}$$

$$\gamma = k_{1z}^s + k_{2z}^s \tag{7}$$

In these equations, $R_F(k)$ is the reflectance of an ideal (smooth) film evaluated for neutrons whose wavevector perpendicular to the film is k, β_f and β_s are the neutron scattering length densities of the film and its substrate respectively, $\rho = (x,y)$ designates the position of a point on the surface of the film, $\xi(\rho)$ is the height of the upper film surface with respect to the average height of this surface, and $\eta(\rho)$ is the height of the lower surface with respect to its mean position. The standard deviations of the heights of the upper and lower surfaces are σ_1 and σ_2.

To evaluate the first two contributions to the diffuse scattering, it is convenient to use a height-height correlation function that is a modified form of that which applies to a self-affine surface. This approximation was introduced by Sinha et al [3]:

$$\langle \xi(\rho) \, \xi(0) \rangle = C(\rho) = \sigma^2 e^{(\rho/\zeta)^{2h}} \tag{8}$$

The Hurst exponent, h, takes values between zero and one, with many natural phenomena falling in the range 0.6 to 0.7. The correlation range, ζ is introduced to prevent the divergence of $C(\rho)$ that occurs for a true self-affine surface. In the calculations presented here, I have taken a value of 10,000 Å for ζ.

3. EXAMPLES OF DIFFUSE SCATTERING PATTERNS

In order to provide some indication of the complexity of diffuse scattering patterns that can be obtained with rough films, I have calculated the various contributions for a (fictitious) system with scattering length densities of $\beta_f = 4 \times 10^{-6}$ Å^{-2} and $\beta_s = 8 \times 10^{-6}$ Å^{-2}, chosen so that the contrast between air and film is the same as that between the film and its substrate. To display the diffuse scattering, I use grey-scale plots, with the dynamic range chosen to enhance the effects of interest. In most cases, the diffuse scattering is mapped in a Cartesian space spanned by q_z and q_x, the components of neutron wavevector transfer that are perpendicular and parallel to the film surface and within the scattering plane. For all calculations I have used a self-affine surface with a Hurst exponent, h, of 0.5 and a film thickness of 400 Å. I consider the various contributions to the diffuse scattering in order—the Newton term, the contribution from the rough lower surface of the film, and finally correlation between the two rough surfaces of the film.

3.1 Newton's Fringes

For small values of the surface roughness, the exponential term in eqn (1) may be expanded to first order in $<\xi(\rho)\,\xi(0)>$ and the F_n defined by eqns (5) can then be combined to yield an approximate expression for the Newton term:

$$\left.\frac{d\sigma}{d\Omega}\right)_{\text{upper}} = (\beta_F)^2\,|1 + R_F(k_{1z})|^2\,|1 + R_F(k_{2z})|^2\, e^{-q_z^2\sigma^2} \int dx \int dy\, e^{-i\vec{k}.\vec{\rho}}\, C(\rho) \qquad (9)$$

It turns out that this approximation is quite good even for values of $q_z\sigma$ approaching unity (cf Figure 1). For larger values, however, eqn (9) overlooks the fact that the Gaussian damping factors in eqn (1) affect the n=1 and n=2 terms most strongly, because $(f_n^2 + g_n^2)\sigma^2$ is largest for these two terms. As a consequence, when σ is large, the contribution to the diffuse scattering from eqn (5a) is more heavily damped than those from eqns (5e) and (5f). Since the latter equations involve oscillating functions ($R_F(k_{1z})$ or $R_F(k_{2z})$), they contribute to fringes of diffuse scattering that are suppressed (though not eliminated) in eqn (9). However, the fact that these fringes are superposed on other contributions to the scattering means that their visibility is low, even when σ is large. They are, in fact, barely discernable in Figure 2.

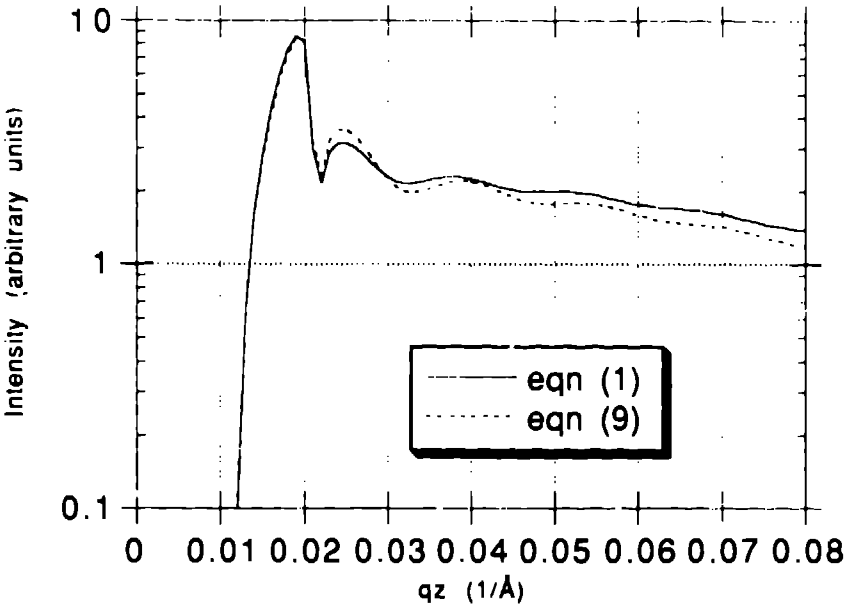

Figure 1: Comparison of the diffuse intensity predicted by eqns (1) and (9) for a 400 Å thick film with $\beta_f = 2 \times 10^{-6}$ Å^{-2}, $\beta_s =$ [illegible] 10^{-6} Å^{-2}, $\sigma = 10$ Å, $q_x = 0.0001$ Å^{-1}

Except for films with rough upper surfaces and smooth lower surfaces, the faint Newton's fringes will probably be difficult to observe. It will probably be easier to detect these fringes in rather perfect periodic multilayer systems with rough air/film interfaces. In this case, the reflectance is enhanced at quasi-Bragg wavevectors and one would expect strong diffuse fringes to emanate from the Bragg peaks. The fringes, which arise from the R_F terms in eqns (5) (principally eqns (5e) and (5f)), should follow loci of constant k_{1z} or constant k_{2z} because it is along these trajectories that the reflectances are constant. Suitable multilayers can be prepared, for example, by annealing certain block copolymer films whose overall thickness is not a multiple of the periodicity generated during microphase separation [4]. These films form good periodic multilayers with islands of polymer at the air/multilayer interface. Indeed, the observation of Newton's fringes, with their characteristic constant-k_{1z} or constant-k_{2z} loci, may provide an easy method for determining the presence and sizes of such surface islands. It is worth noting that Newton's fringes are in registry at $q_x = 0$ with the peaks of the specular scattering.

The most prominent structure in figure 2 arises from the $|1 + R_F(k_{1z})|^2$ and $|1 + R_F(k_{2z})|^2$ terms in eqn (9) in the neighbourhood of the critical edge (which is at $q_z \approx 0.02$ Å for the parameters of Figure 1). As shown in Figure 3, terms of this sort can have considerable structure for values of k_z below the critical edge. However, the form of this structure, and indeed the number of peaks generated, depends on the details of the scattering contrasts and the film thickness. It is conceivable that the enhancement of the diffuse scattering afforded by these pronounced fringes could be used to advantage to extract information about the surface height-height correlation function $C(\rho)$ for the upper surface of suitable films. As eqn (9) demonstrates, the variation of intensity in q_x – which changes along the fringes— is given by the Fourier transform of $<\xi(\rho)\ \xi(0)>$ for small values of $q_z\sigma$.

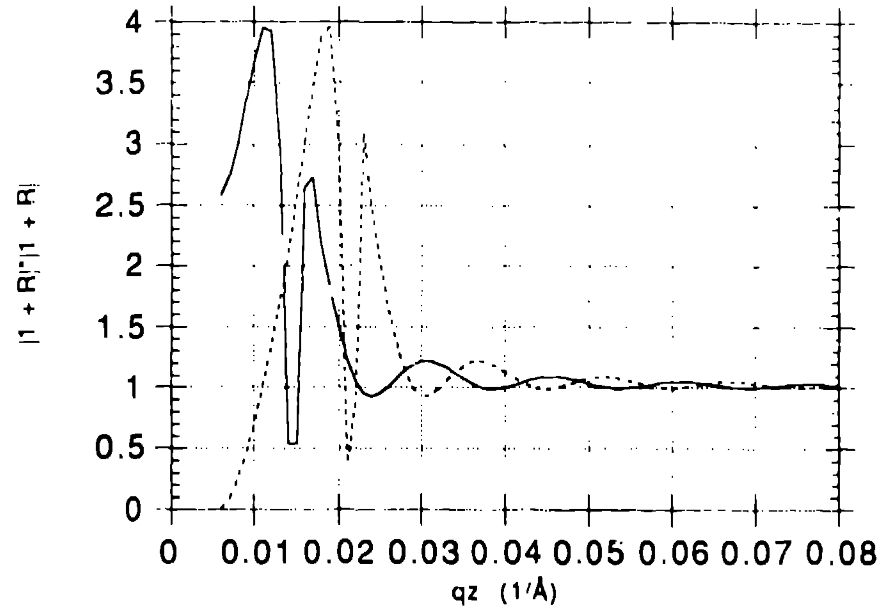

Figure 3: Plot of $|1 + R(k_{1z})|^2$ (solid) and $|1 + R(k_{2z})|^2$ (dotted) for a 400 Å film with $\beta_f = 4 \times 10$ Å^{-2}, $\beta_s = 8 \times 10$ Å^{-2} and $q_x = 0.00005$ Å^{-1}

It is perhaps worth pointing out that the values of q_x probed by diffuse neutron scattering from a surface are very small—less than 0.001 Å^{-1} in a typical grazing incidence experiment. This means that the corresponding minimum length scale within a surface to which neutrons are sensitive is close to a micron. This is the only example I know of in which thermal neutrons measure, by diffraction, structures that can be imaged in real space by optical techniques.

3.2 The Effect of the Film/Substrate Interface

The diffuse scattering contributed by roughness of the film/substrate interface (the lower film surface) is given by eqn (2). For convenience, I have taken the roughness amplitude of this surface and its height-height correlation function to be the same as those used for Figure 2. The resulting diffuse scattering is shown in Figure 4. The two strong fringes are caused by structure in the film transmission function $T_F(k)$ that occurs for values of k close to the critical edge. The details of this structure depend on the scattering length densities and film thickness. Because I have chosen the same scattering contrasts for the air/film and film/substrate interfaces, the low-q_z fringes in Figures 2 and 4 are of similar intensity. In both cases, these intense fringes occur at constant values of k_{1z} or k_{2z}. It is worth noting that scattering from roughness of the lower film surface does not contribute to Newton's fringes because both $T_F(k_{1z})$ and $T_F(k_{2z})$ tend to unity for large values of their arguments—there are no perceptible oscillations.

3.3 The Effect of Correlations between Film Surfaces

The final contribution to the diffuse scattering arises from correlation between the heights of the film's two rough surfaces. When the roughness of the two surfaces is small ($q_z\sigma << 1$), the exponential terms in eqn (3) may be expanded to yield:

$$\left.\frac{d\sigma}{d\Omega}\right)_{corr} = 2\,(\beta_S - \beta_F)(\beta_F)\, e^{-q_z^2(\sigma_1^2+\sigma_2^2)/2}$$
$$\times \mathrm{Re}\left[\int dx \int dy\, e^{-i\vec{\kappa}.\vec{\rho}} \left\langle \eta(\rho)\, \xi(0) \right\rangle T_F(k_{1z}) T_F(k_{2z}) \{1 + R_F^*(k_{1z})\}\{1 + R_F^*(k_{2z})\}\, e^{i\gamma t}\right] \qquad (10)$$

Because of the $e^{i\gamma t}$ factor in eqn (10), this contribution to the diffuse scattering displays oscillations whose period is inversely proportional to the film thickness, t. The resulting fringes occur at regularly spaced values of γ which, except close to the critical edge, implies that the fringes are uniformly separated in q_z. This is shown in Figure 5. Although the diffuse fringes in this Figure coincide with peaks in the specular reflectivity for large values of q_z, registry is not perfect close to the critical edge. In this way, fringes due to correlated roughness differ from Newton's fringes.

The complete diffuse scattering pattern is obtained by adding the contributions from Figures 2, 4, and 5. The result is shown in Figure 6. For the case considered here, the fringes due to correlated roughness completely overwhelm the Newton's fringes, which are no longer visible in the composite pattern. This is likely to be true in general for thin homogeneous films. For periodic multilayers, there is no reason why both types of fringe should not be equally visible because the film reflectance, R_F—which governs the visibility of Newton's fringes—can be large at Bragg positions.

4. IMPERFECT CORRELATIONS BETWEEN ROUGH FILM SURFACES

For thin films of liquids on rough surfaces, and indeed for other types of film, various physical mechanisms tend to cause the upper film surface to conform to the substrate surface for long wavelength height fluctuations and to be smoother than the substrate at shorter wavelengths. Robbins et al [4] have shown that for liquid films one may write:

$$\zeta_L(q_{\|}) = \frac{\zeta_S(q_{\|})\ K(q_{\|})}{1 + q_{\|}^2\ \xi^2} \tag{11}$$

where $\zeta_S(q)$ and $\zeta_L(q)$ are the Fourier components of the height fluctuations of the substrate and liquid surfaces respectively. The healing length, ξ, represents the smoothing effect that surface tension has on the film/air interface and K(q), which decreases as q increases from a value of unity at q = 0, reflects the non-local interaction between the film's surfaces. The $q_{\|}$ vectors in eqn (11) are measured in the plane of the film. Using eqn (11), the correlation function for the heights of the liquid and substrate surfaces can be written in the form:

$$\left\langle \zeta_S(\rho)\ \zeta_L(0) \right\rangle = \sum_q \frac{\left|\zeta_S(q_{\|})\right|^2 K(q_{\|})}{1 + q_{\|}^2\ \xi^2}\ e^{-iq_{\|}\cdot\rho} \tag{12}$$

For cases in which the approximation of eqn (10) is adequate (small amplitude roughness), the above expression allows a straightforward assessment of finite correlation on the diffuse scattering. Scattering from the substrate surface in the absence of the film is described by $\left|\zeta_S(q_{\|})\right|^2$, a function which has the form of a Voigt function for a self affine surface [1]. When a film is added, the diffuse scattering, measured along one of the fringes, will have a shape given by the right hand side of eqn (12). The profile will be more heavily damped than that of the substrate as $q_{\|}$ increases. In a local (Deryagin) approximation in which K(q) = 1, this additional damping is described by the healing length, ξ, which can thus be extracted from the data.

Data analysis for surfaces with large amplitude roughness is more complex, because the correlation function of eqn (12) appears as the argument of an exponential in eqn (3). Nevertheless, it should still be possible to extract the healing length, especially since data from successive diffuse fringes can be combined (to increase statistical accuracy) once the trivial factors (T_F and R_F) have been removed using eqn (3).

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